

Effect of the Octadecyl Acrylate Concentration on the Phase Behavior of Poly(octadecyl acrylate)/Supercritical CO₂ and C₂H₄ at High Pressures

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ABSTRACT: Pressure–composition isotherms were measured for the CO₂/octadecyl acrylate system at 45.0, 80.0, and 100.0°C and at pressures up to 307 bar. This system exhibited type I phase behavior with a continuous mixture-critical curve. The solubility of octadecyl acrylate for the CO₂/octadecyl acrylate system increased as the temperature increased at a constant pressure. The experimental results for the CO₂/octadecyl acrylate system were modeled with the Peng–Robinson equation of state. A good fit of the data was obtained with the Peng–Robinson equation of state with one adjustable parameter for the CO₂/octadecyl acrylate system. Experimental cloud-point data for the poly(octadecyl acrylate)/CO₂/octadecyl acrylate system were measured from 36 to 193°C and at pressures up to 2100 bar, and the added octadecyl acrylate concentrations were 11.9, 25.9, 28.0, 35.0, and 40.0 wt %. Poly(octadecyl acrylate) dissolved in pure CO₂ up to 250°C and 2100 bar. Also, adding 45.0 wt % octadecyl acrylate to the poly(octadecyl acrylate)/CO₂

solution significantly changed the phase behavior. This system changed the pressure–temperature slope of the phase-behavior curves from an upper critical solution temperature (UCST) region to a lower critical solution temperature region as the octadecyl acrylate concentration increased. Cloud-point data to 150°C and 750 bar were examined for poly(octadecyl acrylate)/C₂H₄/octadecyl acrylate mixtures at octadecyl acrylate concentrations of 0.0, 15.0, and 45.0 wt %. The cloud-point curve of the poly(octadecyl acrylate)/C₂H₄ system was relatively flat at 730 bar between 41 and 150°C. The cloud-point curves of 15.0 and 45.0 wt % octadecyl acrylate exhibited positive slopes extending to 35°C and approximately 180 bar. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 372–380, 2002

Key words: phase behavior; supercritical CO₂; CO₂/octadecyl acrylate system; poly(octadecyl acrylate)/CO₂/octadecyl acrylate system

INTRODUCTION

The phase behavior of polymer/supercritical fluid mixtures must be understood for developing new polymer processing technologies and industrial applications. Also, binary monomer/supercritical fluid mixtures are important for a number of applications involving supercritical fluids.

Recently, we demonstrated the possibility of dissolving polar (meth)acrylate polymers in supercritical CO₂ over a large temperature range at modest pressures if a (meth)acrylate monomer was used.^{1,2} For many free-radical polymerization reactions, the time to form a polymer is on the order of seconds, whereas the residence time in the reactor is typically on the order of minutes. A liquid cosolvent can greatly enhance polymer solubility in a given solvent for several reasons. If the solvent is

highly expanded, the addition of a dense, liquid cosolvent reduces the free-volume difference between the polymer and solvent.³ Also, if the cosolvent provides favorable physical interactions, such as polar interactions, the region of miscibility should be expanded.⁴ Interpreting the effect of a cosolvent added to a supercritical fluid (SCF) solvent is slightly more complicated because increasing the system pressure reduces the free-volume difference between the solvent and polymer and increases the probability of interaction for the polymer, solvent, and cosolvent segments in solution.⁵ The high-pressure polymer–SCF solvent–cosolvent studies reported in the literature show that cloud points monotonically decrease in pressure and temperature with the addition of a polar cosolvent as long as the cosolvent does not form a complex with the polar repeat units in the polymer.^{6–8} In these cases, the cosolvency effect is directly related to the polar forces of attraction contributed by the cosolvent and to the increase in solvent density resulting from the addition of a liquid cosolvent to a supercritical fluid solvent.

As a general rule, the cloud-point curve of a mixture consisting of a very polar component, in this case poly(acrylate), and a much less polar component, here

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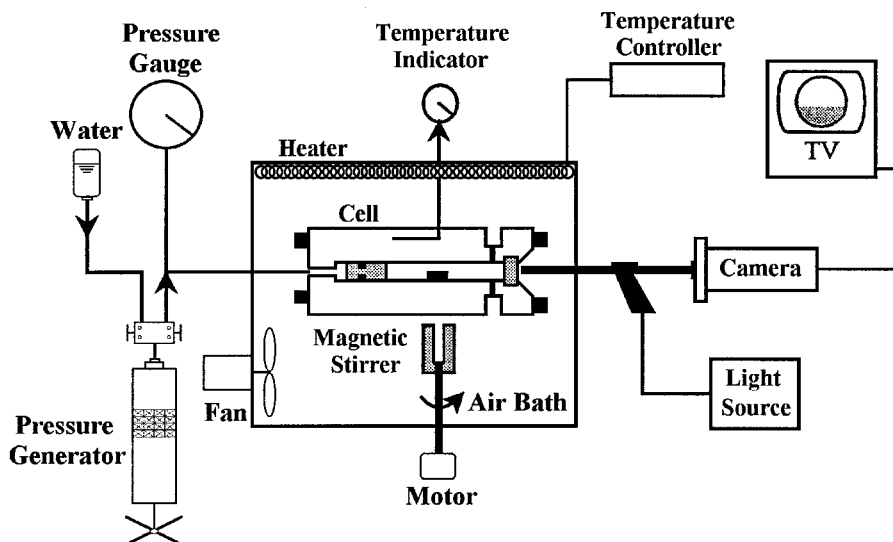


Figure 1 Schematic diagram of the experimental apparatus.

CO₂, exhibits a negative slope in pressure–temperature space. The interchange that characterizes the balance of polymer segment/CO₂ cross interactions relative to polymer segment/segment and CO₂/CO₂ self-interactions is very temperature-sensitive because of the strong polar interactions between polymer segments. At the temperatures at which entropic effects are expected to dominate, the location of the cloud-point curve is more a reflection of the free-volume difference between the dense polymer and the expanded CO₂ than the balance of intermolecular interactions.

Ethylene is expected to exhibit some of the solvent characteristics of CO₂ because ethylene also has a quadrupole moment. Byun et al.⁹ reported that the cloud-point curve for a poly(butyl acrylate) (PBA)/ethylene system was relatively flat at approximately 800 bar and from 65 to 190°C. The phase behavior of the PBA/ethylene system was similar to that of the PBA/CO₂ system, for which the curve was flat at about 1000 bar from 130 to 200°C. The PBA/CO₂ curve showed a sharp increase in pressure at about 80°C, whereas the PBA/ethylene system curve was still flat at the same temperature. PBA remained dissolved in ethylene at lower temperatures because the ethylene was much more polarizable than CO₂ (42.5 vs 27.5 cm³), and the PBA/ethylene dispersion interactions were much stronger.

Experimental phase-behavior data for small amounts of a binary CO₂/octadecyl acrylate system were obtained to complement the poly(octadecyl acrylate)/CO₂/octadecyl acrylate studies presented here because there were no literature phase-behavior data available on this mixture. The primary purpose for obtaining the CO₂/octadecyl acrylate system was to determine whether CO₂ and octadecyl acrylate would form multiple phases in the pressure–temperature–

composition regions explored in the poly(octadecyl acrylate)/CO₂/octadecyl acrylate studies. The experimental data of the CO₂/octadecyl acrylate system were fitted to the Peng–Robinson equation of state,¹⁰ and the phase behavior for this binary solvent mixture was calculated at elevated operating temperatures and pressure.

The focus of this work is presented as the determination of the impact of the octadecyl acrylate cosolvent on the phase behavior of the poly(octadecyl acrylate)/CO₂ system. Because CO₂ is considered a desirable reaction medium for free-radical polymerizations,¹¹ the phase behavior for these ternary poly(octadecyl acrylate)/supercritical CO₂/octadecyl acrylate mixtures provides information needed on the regions in which homogeneous polymerization can occur in the presence of excess monomer. Rindfleisch et al.¹² demonstrated that poly(octadecyl acrylate)/CO₂ cloud-point curves were almost vertical at approximately 1100–2700 bar and high temperatures.

The intermolecular interactions between CO₂ and a poly(octadecyl acrylate) repeat unit are expected to be similar in strength to those between CO₂ and a poly(octadecyl acrylate) repeat unit. Therefore, the difference in the phase behavior is attributed to the different degrees of chain flexibility for these two polymers, which imply a more unfavorable conformational entropy of mixing for poly(octadecyl acrylate).¹² The key issue is how to account for the intrasegmental and intersegmental interactions of the many segments of the polymer relative to the small number of segments in a solvent molecule.

EXPERIMENTAL

Figure 1 shows a schematic diagram of the experimental apparatus used for pressure–composition iso-

TABLE I
Experimental Data for the CO₂/Octadecyl Acrylate
System Measured in This Study

Molar fraction of octadecyl acrylate	Pressure (bar)	Transition
<i>T</i> = 45°C		
0.012	183.6	BP
0.026	182.5	BP
0.038	177.9	BP
0.044	177.9	BP
0.054	179.7	BP
0.069	177.9	BP
0.080	164.5	BP
0.096	149.0	BP
0.106	143.1	BP
0.120	132.1	BP
0.141	108.3	BP
0.163	100.0	BP
0.187	93.8	BP
0.203	90.0	BP
0.242	82.4	BP
0.294	71.7	BP
0.364	58.3	BP
0.434	55.2	BP
0.719	27.9	BP
<i>T</i> = 80°C		
0.016	250.9	DP
0.019	255.9	DP
0.024	256.6	CP
0.030	256.2	BP
0.044	254.8	BP
0.063	247.2	BP
0.074	242.8	BP
0.101	226.6	BP
0.122	211.0	BP
0.160	185.9	BP
0.192	148.3	BP
0.322	102.4	BP
0.434	77.6	BP
0.719	37.9	BP
<i>T</i> = 120°C		
0.018	305.9	DP
0.029	307.0	DP
0.052	307.5	CP
0.080	303.1	BP
0.098	285.9	BP
0.117	267.9	BP
0.147	244.1	BP
0.176	216.9	BP
0.252	179.0	BP
0.434	104.5	BP
0.719	50.4	BP

BP = bubble point; CP = critical point; DP = dew point.

therms for the CO₂/octadecyl acrylate mixtures^{13,14} and obtained cloud-point curves for poly(octadecyl acrylate)/CO₂/octadecyl acrylate ternary mixtures.^{15,16} The bubble-point, dew-point, and cloud-point curves were obtained with a high-pressure, variable-volume cell described in detail elsewhere.¹³⁻¹⁶ Cloud points

were measured for the polymer solutions at a fixed poly(octadecyl acrylate) concentration of 5.0 ± 0.5 wt %, which is typical of the concentrations used for polymer/SCF solvent studies.¹⁷ The polymer was loaded into the cell to ± 0.002 g, and then the cell was purged with nitrogen followed by CO₂ to ensure that all of the air was removed. Liquid octadecyl acrylate was injected into the cell to ± 0.002 g with a syringe, and CO₂ was transferred into the cell gravimetrically to ± 0.004 g with a high-pressure bomb.

The mixture was compressed to the desired pressure with an internal piston displaced with water in a high-pressure generator (HIP Inc., USA, model 37-5.75-60). The pressure of the mixture was measured with a Heise gauge (Dresser Industries, USA, model CM-108952; 0-3450, accurate to ± 3.5 bar). Because the measurement was made on the water side of the piston, a small correction (~ 1 bar) was added to account for the pressure required to move the piston. The temperature in the cell was measured with a platinum-resistance thermometer (Thermometrics Corp., USA, Class A) connected to a digital multimeter (Yokogawa, Japan, model 7563; accurate to $\pm 0.005\%$). The system temperature was typically maintained to $\pm 0.2^\circ\text{C}$ below 200°C . The mixture inside the cell was viewed on a video monitor with a camera coupled to a borescope (Olympus Corp., UK, model F100-038-000-50) placed against the outside of the sapphire window. Light was transmitted into the cell with a fiber optic cable connected at one end to a high-density illuminator (Olympus Optical Co., Japan, model ILK-5) and at the other end to a borescope.

The molar fractions were accurate to ± 0.0025 . Cloud points were measured and reproduced at least twice to ± 2.8 bar and $\pm 0.3^\circ\text{C}$. Bubble-point, dew-point, and critical-point transitions for the CO₂/octadecyl acrylate mixtures were measured and reproduced at least twice to ± 0.5 bar and $\pm 0.2^\circ\text{C}$. The CO₂/octadecyl acrylate molar fractions had estimated accumulation errors of less than $\pm 0.8\%$, except for the data point at 1.0 mol % octadecyl acrylate, which had a slightly higher estimated error of $\pm 1.5\%$.

MATERIALS

CO₂ (99.8% minimum purity) was obtained from Daesung Oxygen Co. and used as received. Poly(octadecyl acrylate) [weight-average molecular weight (M_w) = 93,300, glass-transition temperature = 39.9°C] and octadecyl acrylate (99% purity) were obtained from Aldrich Co. and used as received. To prevent octadecyl acrylate polymerization, we used 2,6-di-*tert*-butyl-4-methyl phenol (Aldrich; 99% purity) as an inhibitor at a concentration of 0.005 times the amount of octadecyl acrylate.

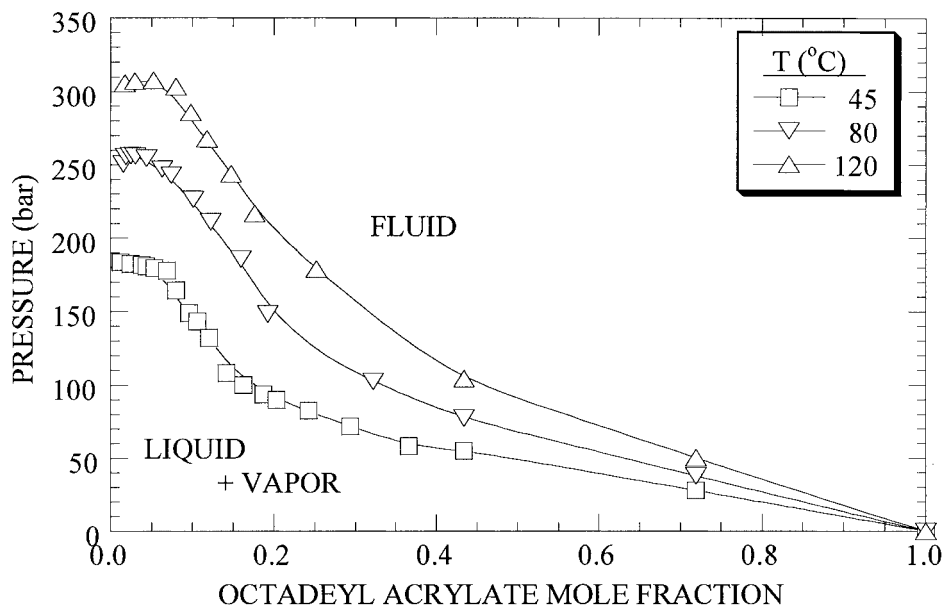


Figure 2 Experimental isotherms for the CO₂/octadecyl acrylate system at 45, 80, and 120°C.

RESULTS AND DISCUSSION

Phase behavior of the CO₂/octadecyl acrylate mixture

Table I and Figure 2 present the CO₂/octadecyl acrylate system experimental data obtained in this study. Each data point for the CO₂/octadecyl acrylate system was reproduced to ± 0.5 bar at least twice for a given loading of the cell. Each isotherm was constructed from data taken from several independent loadings of the cell. The molar fractions were accurate to ± 0.0025 . Figure 2 shows the experimental pressure–composition (P - x) isotherms at 45, 80, and 120°C and at pressures up to 307 bar. The P - x isotherms shown in Figure 2 are consistent with those expected for a type I system,^{18,19} in which a maximum occurs in the continuous mixture-critical curve. A three-phase, liquid–liquid–vapor equilibrium was not observed under these conditions. The behavior exhibited by the CO₂/octadecyl acrylate system was consistent with that of the CO₂/butyl acrylate,¹ CO₂/butyl methacrylate,² ethylene/methyl acrylate,²⁰ and ethylene/vinyl acetate systems.²¹ The bubble-point portion of the P - x isotherms for the CO₂/octadecyl acrylate system are convex toward lower pressures; this means that CO₂ was very miscible in the octadecyl acrylate-rich liquid phase. The high solubility of CO₂ in the octadecyl acrylate-rich liquid was probably due to the formation of a weak complex between octadecyl acrylate and CO₂. Kazarian et al.²² showed that the carbon atom of CO₂ acts as an electron acceptor that complexes with the carbonyl oxygen of poly(octadecyl acrylate); therefore, the same behavior can be reasonably expected for CO₂ with octadecyl acrylate monomer.

The experimental data obtained in this work were modeled with the Peng–Robinson equation of state. The equation of state is briefly described here. The Peng–Robinson equation of state¹⁰ is used with the following mixing rules:

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij})$$

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij}$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})(1 - \eta_{ij})]$$

where k_{ij} and η_{ij} are interaction binary parameters that are determined by the fitting of pressure–composition data and a_{ii} and b_{ii} are pure component parameters defined by Peng and Robinson.¹⁰ The expression for the fugacity coefficient with these mixing rules was given by McHugh and Krukoni¹⁹ and is not reproduced here. Table II lists the pure component critical temperatures, critical pressures, and acentric factors

TABLE II
Pure Component Parameters Used with the Peng–Robinson Equation of State

Component	T_c (°C)	P_c (bar)	Acentric factor
Carbon dioxide	31.1	73.9	0.225
Octadecyl acrylate	632.6	9.83	0.818

P_c = critical pressure; T_c = critical temperature.

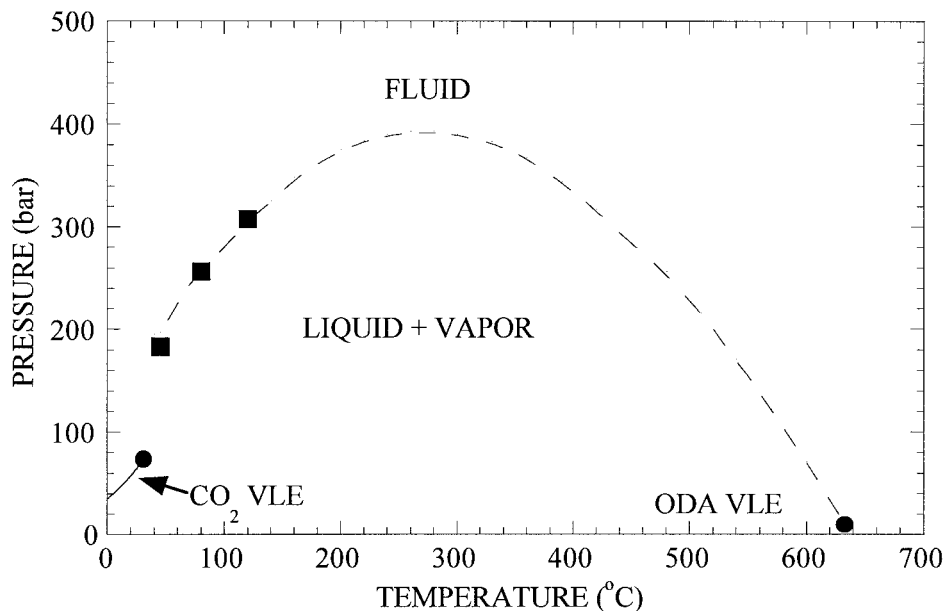


Figure 4 Pressure–temperature diagram for the CO₂/octadecyl acrylate system. The solid lines and solid circles represent the vapor liquid lines and the critical points for pure CO₂ and octadecyl acrylate. The solid squares are mixture-critical points determined from isotherms measured in this study. The dashed lines represent calculations obtained with the Peng–Robinson equation of state ($k_{ij} = 0.053$).

for CO₂/octadecyl acrylate used with the Peng–Robinson equation of state.

Figure 3 shows a comparison of experimental results and calculated P - x isotherms at 45.0 and 120.0°C for the CO₂/octadecyl acrylate system with the optimized values of k_{ij} and η_{ij} determined at 80°C. A good fit of the data was obtained with the Peng–Robinson equation with one adjustable mixture parameter for the CO₂/octadecyl acrylate system.

Figure 4 shows the mixture-critical curve for the CO₂/octadecyl acrylate system predicted by the Peng–Robinson equation of state. The calculated mixture-critical curve is type I, in agreement with experimental observations. As shown in Figure 4, the solid lines represent the vapor pressure for pure CO₂²³ and octadecyl acrylate.^{24,25} The solid circles represent the critical point for pure CO₂ and octadecyl acrylate.^{24,25} The upper part of the dashed line is single-

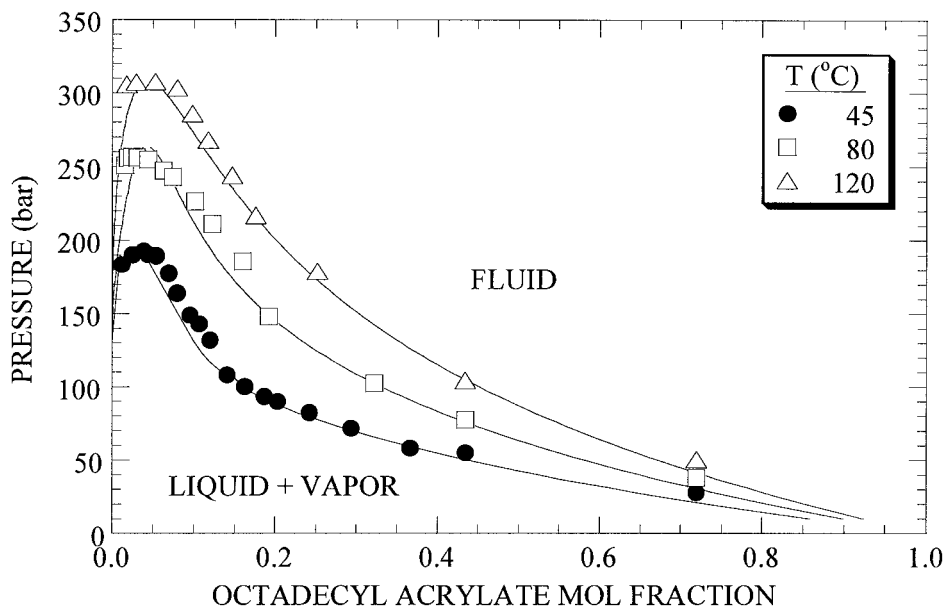


Figure 3 Comparison of the experimental data (symbols) for the CO₂/octadecyl acrylate system and calculations (solid lines) obtained with the Peng–Robinson equation of state ($k_{ij} = 0.053$).

TABLE III
Experimental Cloud-Point Data for the Poly(octadecyl acrylate) (PODA)/CO₂ Octadecyl Acrylate (ODA) System Measured in This Study

<i>T</i> (°C)	<i>P</i> (bar)
4.9 wt % PODA + 11.9 wt % ODA	
143.5	2100.0
144.3	1752.1
145.1	1631.4
147.3	1408.6
149.1	1309.3
170.6	1012.4
193.8	922.8
5.2 wt % PODA + 25.8 wt % ODA	
79.3	1560.0
81.1	870.0
85.3	744.1
108.3	594.8
128.6	558.3
150.4	550.0
4.8 wt % PODA + 28.7 wt % ODA	
60.0	1656.9
61.2	1119.0
65.3	698.3
70.3	622.4
72.8	594.8
90.0	504.1
111.3	474.5
134.5	482.8
155.6	488.3
4.7 wt % PODA + 35.0 wt % ODA	
40.5	332.8
60.1	281.0
79.8	286.6
99.4	312.1
4.1 wt % PODA + 40.0 wt % ODA	
36.3	158.6
40.8	167.2
46.6	179.0
52.1	190.0
69.6	223.5
81.6	247.9
90.9	264.1
99.7	277.9
108.1	291.4
118.4	305.2
137.8	326.2
158.9	346.6

phase (fluid), and the lower part is two-phase (vapor and liquid). The solid squares are the mixture-critical points determined from isotherms measured in this experiment. The dashed lines represent the calculated value obtained with the Peng–Robinson equation of state.

Cloud-point behavior of the poly(octadecyl acrylate)/CO₂ (or C₂H₄)/octadecyl acrylate system

Table III and Figure 5 show the cloud-point behavior of the poly(octadecyl acrylate)/CO₂/octadecyl acrylate mixture obtained in this study. With 11.9 wt % octadecyl acrylate added to the solution, the cloud-

point curve exhibits upper critical solution temperature (UCST) phase behavior with a negative slope. With 25.8 wt % octadecyl acrylate in solution, the cloud-point pressure remained virtually constant at 500 bar over a temperature range of 80–150°C. With 28.0 wt % octadecyl acrylate added to the solution, the cloud-point curve exhibits U-LCST phase behavior from a positive slope at low pressures to a negative slope that rapidly increases at 70°C. The effect of the octadecyl acrylate cosolvent on the phase behavior was similar to that observed for the PBA/CO₂/butyl acrylate¹ and poly(ethyl methacrylate)/CO₂/ethyl methacrylate systems.² The slope of the 48.4 wt % octadecyl acrylate curve is 2.9 bar/°C, which is very close to the slope found for the PBA/CO₂/32 wt % butyl acrylate curve.¹ These slopes are approximately 40% greater than those observed for binary poly-(isobutylene)/alkane mixtures reported by Zeman and Patterson;²⁵ this is due to the enhanced influence of hydrostatic pressure on the free-volume difference between poly(octadecyl acrylate) and the CO₂/octadecyl acrylate mixture. The alkanes used by Zeman and Patterson were less compressible than the CO₂/octadecyl acrylate solutions used here. Even though the poly(octadecyl acrylate)/CO₂/octadecyl acrylate curve extends to 40°C, bubble points can be observed, which imply that the cloud-point curve will intersect the liquid–liquid–vapor curve at a much lower temperature.¹⁹ Finally, the effect of the octadecyl acrylate cosolvent on the location of the cloud-point curve diminished in a nonlinear fashion as more octadecyl acrylate was added to the solution. This diminishing-return effect was also seen with the PBA/CO₂/butyl acrylate and poly(ethyl methacrylate)/CO₂/ethyl methacrylate systems. With 45.0 wt % octadecyl acrylate added to the poly(octadecyl acrylate)/CO₂ solution, the cloud-point curve shown in Figure 6 and Table IV takes on the typical appearance of a lower critical solution temperature (LCST) boundary. At 130°C, the phase boundary shifts from 320 to 284 bar with the concentration of octadecyl acrylate increasing from 40 to 45 wt %. The poly(octadecyl acrylate)/CO₂/45.0 wt % octadecyl acrylate phase-behavior curve intersects a liquid → liquid + vapor curve at approximately 40°C and approximately 120 bar. Liquid and vapor phases coexist at pressures below this curve, and the liquid → liquid + vapor curve switches to a liquid₁–liquid₂–vapor curve at temperatures greater than about 40°C. The initial slope of the poly(octadecyl acrylate)/CO₂/octadecyl acrylate LCST curve at the lowest pressures is approximately 1.7 bar/°C. The results obtained in this study clearly demonstrate that it is possible to obtain a single phase that extends over modest pressures with supercritical CO₂ as long as sufficient amounts of free octadecyl acrylate monomer are present in the solution.

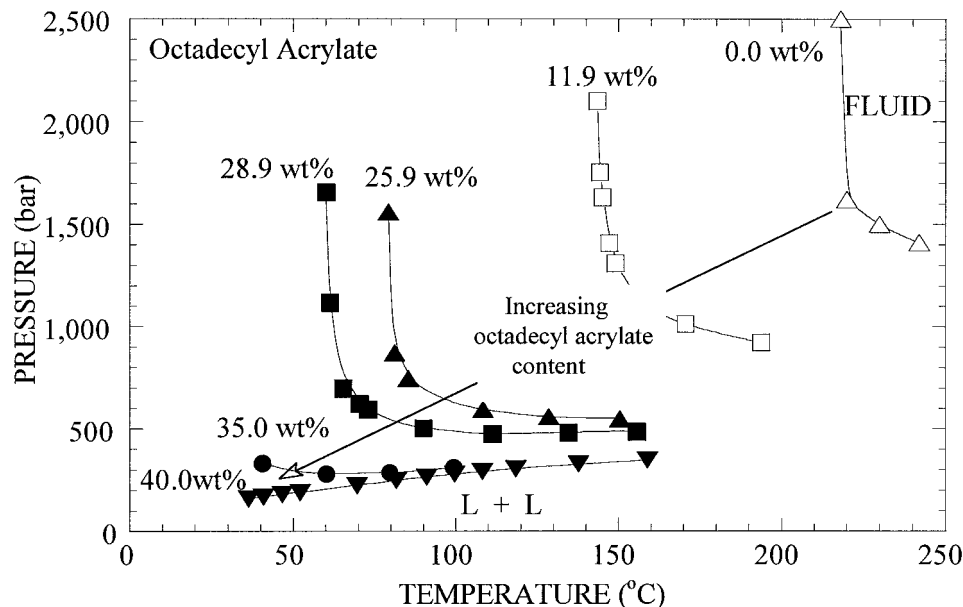


Figure 5 Experimental cloud-point curves for poly(octadecyl acrylate)/CO₂/octadecyl acrylate systems with different octadecyl acrylate concentrations. The concentration of poly(octadecyl acrylate) was 5.0 ± 1.0 wt % for these data.

Figure 7 and Table V show the cloud-point curve of the poly(octadecyl acrylate)/C₂H₄/0.0, 15.1, and 45.2 wt % octadecyl acrylate system. The poly(octadecyl acrylate) ($M_w = 93,300$)/C₂H₄ data obtained in this study are very close to those of Rindfleisch et al. ($M_w = 23,300$).¹² With 15.1 and 45.2 wt % octadecyl acrylate added to the solution, the cloud-point curve exhibits LCST phase behavior with a positive slope. For the poly(octadecyl acrylate)/C₂H₄ in solution, the cloud-point pressure remained virtually con-

stant at approximately 800 bar over a temperature range of 40–150°C.

CONCLUSIONS

The CO₂/octadecyl acrylate system exhibits type I phase behavior characterized by an uninterrupted mixture-critical curve. The P - x bubble-point curves are convex; this indicates that CO₂ has high solubility

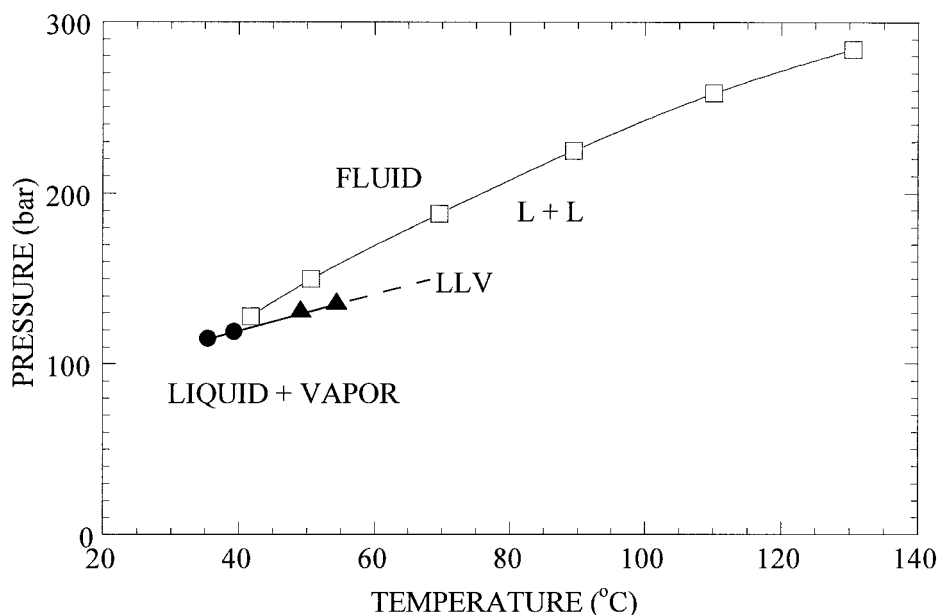


Figure 6 Impact of 45.0 wt % octadecyl acrylate monomer (on a polymer-free basis) on the phase behavior of the poly(octadecyl acrylate)/CO₂ system: (□) fluid → liquid + liquid transition, (●) fluid → liquid + vapor transition, (▲) liquid + liquid → liquid₁ + liquid₂ + vapor (LLV) transition, and (–) suggested extension of the LLV line.

TABLE IV
Experimental CP, BP, and LLV Data for the Poly(octadecyl acrylate) (PODA)/CO₂/Octadecyl Acrylate (ODA) System Measured in This Study

T (°C)	P (bar)	Transition
4.9 wt % PODA + 45.0 wt % ODA		
41.8	127.9	CP
50.7	150.0	CP
69.6	187.9	CP
89.4	224.8	CP
110.1	258.3	CP
130.5	284.1	CP
35.4	115.3	BP
39.3	119.1	BP
49.1	132.2	LLV
54.4	137.0	LLV

BP = bubble point; CP = cloud point; LLV = liquid-liquid-vapor point.

in octadecyl acrylate, probably because of the formation of a weak complex between the carboxylic oxygen in octadecyl acrylate and the carbon in CO₂. The Peng–Robinson equation of state can be used with one adjustable parameter to calculate a reasonable representation of the phase behavior of the CO₂/octadecyl acrylate system. With a single, temperature-independent interaction parameter, quantitative agreement can be obtained between experimental data and calculated phase behavior.

The phase-behavior data for the poly(octadecyl acrylate)/CO₂/octadecyl acrylate system were measured with octadecyl acrylate concentrations of 11.9, 25.8, 28.7, 35.0, and 40.0 wt %. This system changes the pressure–temperature slope of the phase-behavior

TABLE V
Experimental Cloud-Point Data for the Poly(octadecyl acrylate) (PODA)/C₂H₄ Octadecyl Acrylate (ODA) System Measured in This Study

T (°C)	P (bar)
5.1 wt % PODA + 0.0 wt % ODA	
41.3	750.0
51.1	739.7
68.9	730.7
91.4	726.6
110.7	723.8
129.5	724.5
150.8	725.9
5.0 wt % PODA + 15.1 wt % ODA	
40.9	515.9
51.0	522.1
70.3	539.3
90.5	545.9
110.9	563.1
130.7	574.8
154.3	584.8
5.7 wt % PODA + 45.2 wt % ODA	
35.2	181.7
40.8	189.7
61.0	223.6
80.0	248.3
100.9	271.7
119.1	293.1
138.0	312.8

curves from a U-LCST region to an LCST region as the octadecyl acrylate concentration increases. Cloud-point data were obtained for poly(octadecyl acrylate)/C₂H₄/octadecyl acrylate mixtures with octadecyl acrylate concentrations of 0.0, 15.1, and 45.2 wt %. The cloud-point curve of the poly(octadecyl acrylate)/

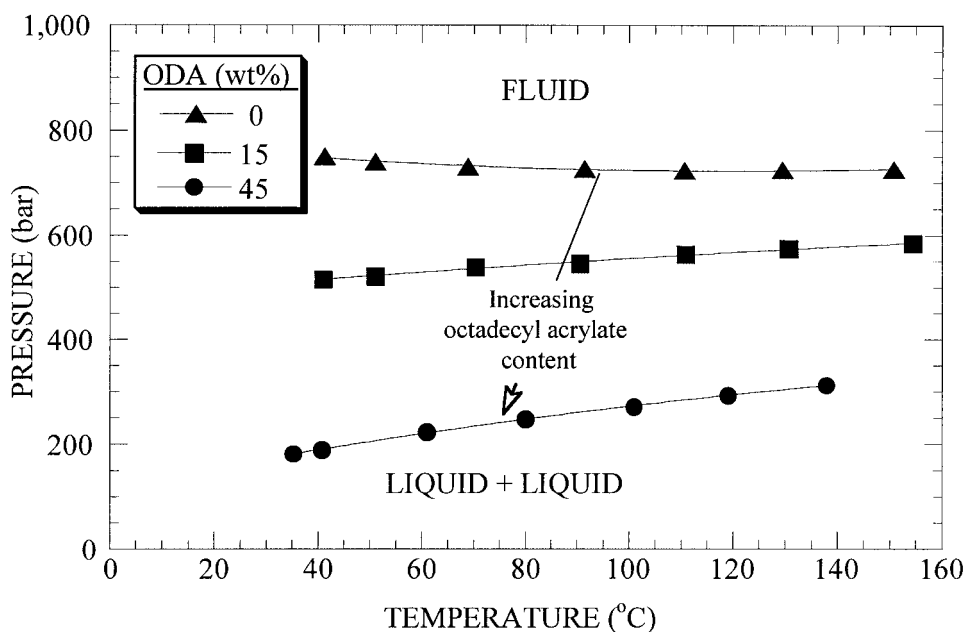


Figure 7 Experimental cloud-point curves for poly(octadecyl acrylate)/C₂H₄/octadecyl acrylate systems with different octadecyl acrylate concentrations. The concentration of poly(octadecyl acrylate) was 5.0 ± 0.5 wt % for these data.

C₂H₄ system is relatively flat at 730 bar for temperatures between 41 and 150°C. With 15.0 and 45.0 wt % octadecyl acrylate, the cloud-point curve exhibits a positive slope that extends to 35°C and approximately 180 bar.

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